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IODINE IN MARINE SAMPLES

Determination of Iodine and Iodine Compounds in Marine Samples by ICPMS and HPLC-ICPMS

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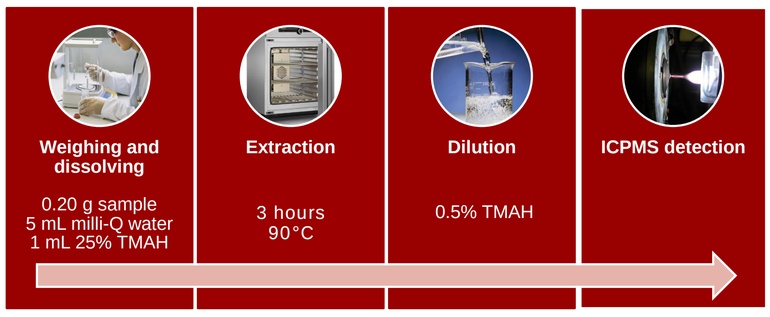
INTRODUCTION

Iodine is an essential element for the human body, why the World Health Organization (WHO) has issued a recommendation that adults should have an intake of 150 µg of iodine/day[1]. Despite this recommendation, it is estimated that 2 billion people worldwide are at risk of developing diseases related to iodine deficiency[2]. A less common iodine related disease is iodine excess, which is defined to an iodine intake larger than 600 µg iodine/day[3]. In Denmark, analyses previously indicated a iodine deficiency in the population, but in recent years, the intake has increased[4]. This could be due recommendations of higher intake of fish, which is a good iodine source. Along with fish, seaweed is considered to be a good iodine source.

Previously it has only been the total iodine concentrations that has been measured and not the various iodine compounds, which may have different bioavailability and toxicity. Therefore, there is an increased interest in the development of analytical techniques for the determination of the different iodine compounds.

TOTAL IODINE CONTENT

PROCEDURE



The results for the fish and shellfish showed that shellfish contained higher concentrations of iodine (2.4-40 µg/g) compared with the fish (0.23-7.7 µg/g). In Fig. 2 iodine concentrations are presented together with typical literature values. There was a large difference between these values. This difference could be due to the growth environment.

The results for the seaweed samples showed a larger variety in the iodine concentrations (0.51-8400 µg/g). Fig. 3 shows the concentration for some of the analyzed samples compared with typical literature values. The values found are in general within the range of the values found in the literature. Some values are below average literature values and some are above average literature values.

RESULTS FOR FISH AND SHELLFISH

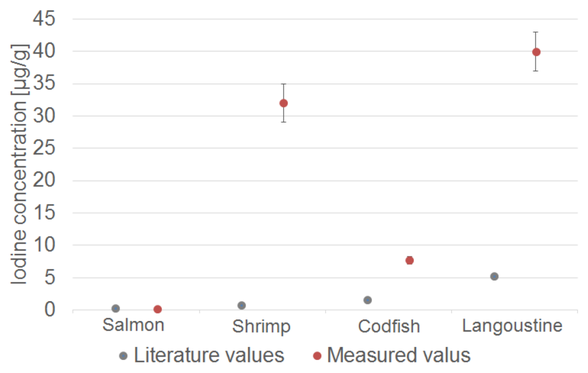


Figure 2. Determination of the total iodine contents in fish and shellfish samples compared with literature values (dry weight). Error lines are shown for 2 SD corresponding to a 95% confidence interval. LOD_{method} = 0.03 µg/g.

RESULTS FOR SEAWEED

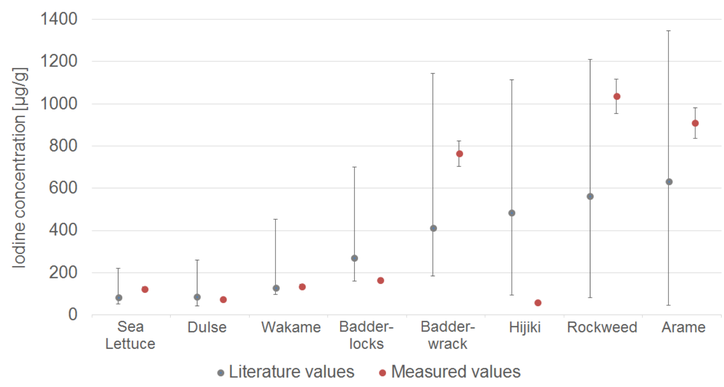


Figure 3. Determination of the total iodine content in seaweed samples compared with literature values (dry weight). Measured values are shown with error lines for 2 SD corresponding to a 95% confidence interval. Literature values are shown with error lines for the total range of measured values. LOD_{method} = 0.03 µg/g.

TOTAL EXTRACTION

An experiment to find the most precise and accurate method for total iodine extraction was conducted. Five different methods were tested and the results (Fig. 1) showed that the 15 minutes extraction with ultrasound gave low yields. The 24 hours extraction at 25°C showed varying results and low precision. Finally the extraction at 90°C for 3 hours was chosen based on the best precision and accuracy.

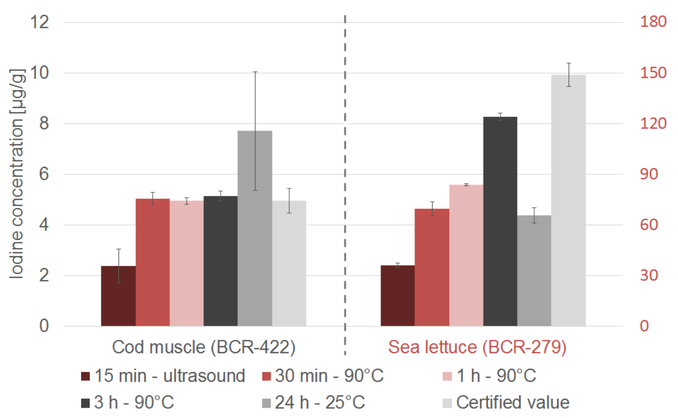


Figure 1. Determination of the total iodine content in two reference materials by five different extraction methods (dry weight). 2SD corresponding to a 95% confidence interval is shown by error lines. LOD_{method} = 0.06 µg/g.

IODINE COMPOUNDS

PROCEDURE

RESULTS FOR CODFISH

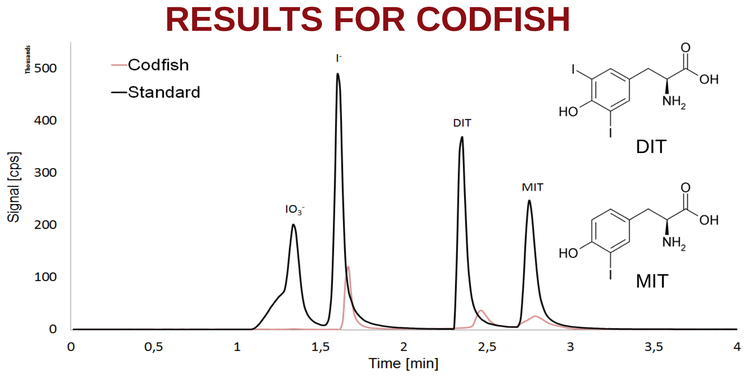


Figure 4. Overlaid HPLC-ICPMS chromatograms of diluted (x10) codfish and standards (50 µg/L) containing four iodine species: iodate, iodide, DIT and MIT. Injection volume: 5 µL – Buffer: 2 mM TEAH/10 mM L-phenylalanine/1% methanole (pH 8) – Flow: 0.30 mL/min.

Thirty-two marine samples were extracted with the enzyme pancreatin (extraction efficiency: 37-94%) and then analyzed by using a reversed phase column in a HPLC-ICPMS system. This method showed a good separation of four iodine species within 3.5 minutes (Fig. 4).

The results showed that all the samples contained iodide (I^-) and diiodotyrosine (DIT) with iodide as the most significant species. The results also showed a great variation in the distribution of monoiodotyrosine (MIT) and iodate (IO_3^-) in the samples.

The samples were not quantified because it was observed that a small amount of the previous sample was transferred to the next measurement. This may have occurred due to insufficient cleaning of the needle in the HPLC autosampler.

SAMPLES

SEAWEED

Twenty-four different seaweed samples were collected containing different seaweed species from different geographical areas.

FISH

Thirteen fish and shellfish samples from the a Norwegian marine powder company were analyzed.

DIET EXAMPLE

Male (DK) example	Intake *[g/day]*	I conc. *[µg/g]*	I intake *[µg/day]*
Fish – Cod	12	3	35
Fish – Salmon	12	0.23	3
Meat[5]	140	0.05	7
Milk[5]	349	0.05	17
Bread[5]	245	0.06	15
Fruit[5]	251	0.02	5
Vegetables[5]	150	0.03	5
Salt (DK) [6]	10	10	100
TOTAL			**186**

Seaweed examples	Intake *[g/day]*	I conc. *[µg/g]*	I intake *[µg/day]*
Green nori	0.5	66	33
Spiral wrack	0.5	600	300
Seaweed (NO)	0.5	4100	2050
Sugar kelp	0.5	8400	4200

The example is based on a Danish male adult and shows a mild iodine excess. These calculations are based on the assumption that the iodine has 100% bioavailability. More likely the bioavailability is 10-20%. To make any recommendations a more thorough investigation of the bioavailability should be conducted.

CONCLUSION

- The most precise and accurate extraction for total iodine was 3 hours at 90°C
- The fish and shellfish samples had iodine concentrations between 0.23-40 µg/g
- The seaweed samples had iodine concentrations between 0.51-8400 µg/g
- All the marine samples contained iodide and DIT
- Noteable variation was found in the distribution of iodate and MIT in the samples

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